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REACTIONS OF n-PROPANOL ON ALUMINA SUPPORTED CHROMIA CATALYST

by

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A THESIS

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ABSTRACT

Studies have been made to investigate the possibility of producing diethyl ketone from n-propanol in a fixed bed reactor using chromia on alumina catalyst.

The experimental equipment consisted of a 2-inch I.D. stainless steel reactor with auxiliary assemblies for liquid feed, preheater, product collection and temperature measurement. A constant catalyst bed height of 8 inches was used and the temperature and n-propanol feed rate were varied over the ranges 300 to 455°C and 1.8 to 5.87 gm moles/hour respectively. Chromatographic analytical methods were used for quantitative determination of reaction products.

Experiments with α- and γ-alumina showed them both to be very active for the dehydration of n-propanol. A chromia on γ-alumina catalyst containing 7.7% Cr_2O_3 prepared in the laboratory was found to dehydrate n-propanol without any formation of diethyl ketone. Incorporating 3.2% sodium in this catalyst almost completely suppressed the dehydrating activity of the catalyst and simultaneously resulted in the formation of diethyl ketone. At 455°C a 96.8% conversion of n-propanol was achieved, although the yield of diethyl ketone was only 15.2%.

As a result of this work it may be recommended that further work be carried out to improve the selectivity of the catalyst. This might be accomplished by finding a catalyst support that is inactive to n-propanol. Also, more suitable equipment should be built so that a range of space velocities and higher temperatures can be studied.

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I - INTRODUCTION

Production of diethyl ketone from n-propanol is of commercial importance in that it has a specific use as a solvent for cellulose esters, cellulose ethers and can be used in de-waxing of lubricating oils.

Komarewsky and Coley[18] report that primary alcohols containing n carbon atoms can be converted into symmetrical ketones containing 2n-1 carbon atoms using chromia as a catalyst. They obtained diethyl ketone from n-propanol using unsupported chromia catalyst in a fixed bed. At a temperature of 425°C the ketone yield was 48.8% of the theoretical and 5.2% of n-propanol was unconverted.

Tollefson[25] investigated this reaction in a fluidized bed using zinc oxide catalyst supported on alumina. A diethyl ketone yield of 14.0% was obtained at 522°C, and unconverted n-propanol was 4.9%.

Hansen[12] studied the same reaction in a fluidized bed using chromia catalyst supported on alumina with the objective of incorporating the advantages of a fluidized bed with those of a supported catalyst. The maximum yield of diethyl ketone obtained in this study was 8.7% at a temperature of 475°C, unconverted n-propanol being 31.2%.

A comparison of Hansen's and Komarewsky's work indicates that the discrepancy in the two results may be due to the difference between the method of catalyst preparation and the fact that Hansen used a supported catalyst. The desirability of using a fluidized bed arises out of its better heat transfer characteristics particularly for an endothermic reaction like the one under consideration. While precipitated chromium oxide is not suitable for fluidized beds, the presence of a support may adversely affect the catalytic activity. Consequently it was decided to study this reaction with particular emphasis on the method of catalyst preparation and choice of support.

II - LITERATURE SURVEY

Chemistry of the Process

Komarewsky and Coley[18] report that in the presence of chromia catalyst primary alcohols of n-carbon atoms are converted to 2n-1 symmetrical ketones by the following mechanism: -

1. Dehydrogenation of primary alcohol to aldehyde.
2. Aldol condensation of the aldehyde.
3. Removal of carbon monoxide from the -CHO group of the aldol leaving a secondary alcohol - decarbonylation.
4. Dehydrogenation of secondary alcohol to ketone.

For n-propanol the chemical equations can be written as

$$2CH_3CH_2CH_2OH \longrightarrow 2CH_3CH_2CHO + 2H_2 \qquad (1)$$

$$CH_3CH_2CHO + CH_3CH_2CHO \longrightarrow CH_3 - CH_2 - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}} - \overset{\overset{O}{\|}}{\underset{\underset{H}{\diagdown}}{C}} \qquad (2)$$

$$CH_3 - CH_2 - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}} - \overset{\overset{O}{\|}}{\underset{\underset{H}{\diagdown}}{C}} \longrightarrow CH_3CH_2CH(OH)CH_2CH_3 + CO \qquad (3)$$

$$CH_3CH_2CH(OH)CH_2CH_3 \longrightarrow CH_3CH_2COCH_2CH_3 + H_2 \qquad (4)$$

The overall reaction may be written as

$$2CH_3CH_2CH_2OH \longrightarrow CH_3CH_2COCH_2CH_3 + 3H_2 + CO \qquad (5)$$

$\triangle H_{298}$ for reactions 1 and 5 are 12.02 and 33.0 k cals/mole respectively[12].

It was found that aldehydes undergo the same type of condensation producing ketones in yields considerably superior to those obtained from the corresponding alcohols. When the aldols of n-butyraldehyde and n-heptaldehyde were subjected to the same reaction conditions excellent yields of ketones were produced directly by a catalytic decomposition reaction. The order of conversion of the reactants to ketones was aldol > aldehyde > alcohol. Further work using tracer technique supported the above mechanism.

Available information on the above individual reactions may be summarized as follows:

1. Dehydrogenation of primary alcohols:-

Studies on catalytic dehydrogenation of primary alcohols to yield aldehydes were started by Ipatieff[14] in 1900. Using chromium, manganese, iron, cobalt, nickel, copper, zinc and their oxides he claimed zinc and brass to be the best catalysts for aldehydic decomposition of alcohols. Since then a large amount of published information has appeared mostly in the patent literature. Most standard works[2] include extensive information on this reaction. While some of the published work is of a contradictory nature the catalysts generally found suitable for this reaction are based on copper, chromium and zinc oxides as active components.

2. Aldol condensation:-

The limited amount of published information on this reaction is of a qualitative nature. Aldehydes are known to give aldols on condensation. Both acids and bases can catalyse the reaction though alkalis (alkali bicarbonates, alkali carbonates, alkali acetates, dilute sodium hydroxide) are claimed[15] to be more effective.

Coley and Komarewsky[5] noted that a sodium hydroxide-precipitated chromia catalyst was quite active in contrast to a comparatively inactive ammonia-precipitated catalyst. Their study on the effect of sodium content on the dehydrogenation - condensation reaction indicated a definite effect on the catalytic activity of the catalyst. Optimum sodium content was found to be 1%. Effect of sodium on catalyst activity is regarded to be consistent with the aldol mechanism.

3. Decarbonylation of aldol:-

There is no available information on this reaction except that implied in Komarewsky and Coley's work[18]. Tollefson[25] did not detect any secondary alcohol though he reports this reaction to be necessary to explain the formation of CO and amylene. Amylene can be obtained by dehydration of diethyl alcohol. He claims that diethyl alcohol is readily dehydrogenated to diethyl ketone the latter having been separated by chromatography and identified by the mass spectrometer.

4. Dehydrogenation of secondary alcohol:-

Catalytic dehydrogenation of secondary alcohols to give ketones is covered in most standard books. Production of acetone from isopropanol and methyl-ethyl ketone from isobutanol is commercially carried out. Most successful catalysts are zinc oxide and brass.

An interesting aspect brought out by this reaction mechanism when chromia is used as a catalyst is that while so far chromia has been used as a catalyst for dehydrogenation of alcohols and straight chain hydrocarbons (e.g., butadiene production) and dehydrocyclisation of n-hexane and n-heptane (involving dehydrogenation and ring closure), in the present reaction it seems to act as a polyfunctional catalyst affecting dehydrogenation, condensation and decarbonylation.

Chromia as a Catalyst

The factors that determine the catalytic activity of a particular preparation are not too well understood. In general, chemical composition alone is not a sufficient criterion of the catalytic activity of a preparation. In many cases physical factors like surface area, pore size and crystal structure determine catalyst activity and selectivity for a particular

reaction. For commercial exploitation a catalyst should also be mechanically strong, chemically stable and inert to poisons or capable of regeneration. While catalyst development and preparation is essentially an art some useful information may be obtained by a careful literature survey. Some of the more pertinent literature information on chromia catalyst with a view to obtain general guiding principles for catalyst preparation is presented below.

Chromium is a transition element of the group VI B of the periodic table. It acts with oxidation states of +2, +3 and +6. Well known oxides of chromium are CrO, chromous oxide; Cr_2O_3, chromic oxide and CrO_3, chromium trioxide. Various intermediate oxides have been reported in the literature. Thermodynamic considerations[26] reveal that Cr_2O_3 cannot be reduced to CrO and Cr in the bulk phase. Oxidation of Cr_2O_3 in air at high temperatures is rather complicated and oxides intermediate between chromic oxide and chromium trioxide may be obtained under certain conditions. It has been pointed out that conditions on surfaces may be different from those for the bulk phase.

Chromic oxide was used in organic dehydrogenation catalysis in its early days by Ipatieff[14]. He reports that chromium causes only slight aldehydic decomposition of alcohols even at high temperatures. Sabatier[19] is reported to have

listed chromium oxide as a catalyst of mediocre activity for the dehydrogenation and dehydration of alcohol with the latter reaction predominating. Lazier and Vaughan[19] studied the catalytic properties of chromium oxide with reference to hydrogenation of ethylene, dehydrogenation of cyclohexane, dehydrogenation and dehydration of ethanol. A number of preparations using different chromium salts and precipitating agents were investigated. The conversion obtained with successive preparations was found to vary from 2 to 80%. It was concluded that while the starting chromium salt and preparation conditions have little to do with catalytic activity x-ray analysis of different preparations showed the amorphous form to be very active as compared to the practically inactive crystalline form.

Weiser[27] reports that many freshly prepared hydrous oxides when heated to about 500°C evolve enough heat to cause the whole mass to become incandescent. This behaviour has been termed glow phenomenon. This phenomenon may result in the transformation of an amorphous form to a crystalline one and/or result in a sudden reduction in surface area. Lazier et al[19] found that glow results in a change from amorphous to crystalline form and is accompanied by a considerable decrease in catalyst activity and sometimes a complete loss thereof. Glow phenomenon was found to be independent of the source of oxide, method of

preparation and atmosphere surrounding the oxide; both gel type structure and powdery chromium oxide exhibited the glow phenomenon. Their studies on oxidation and reduction of the catalyst showed reduced catalysts to be very active in some cases and oxidized catalysts to be inactive in some cases but in general the results were inconclusive.

Work[19] on the decomposition of ethanol on chromia catalyst resulted in simultaneous dehydration and dehydrogenation. Sabatier's work on the decomposition of alcohol on chromia catalyst gave a dehydration - dehydrogenation ratio of 10 as compared to 1.1 obtained by Lazier et al[19]. Glow phenomenon is reported to impair the catalyst activity for alcohol decomposition but not to the same extent as for hydrogenation of ethylene.

Komarewsky and Coley[17] prepared chromia catalyst by four different methods. Catalyst 1 was prepared by the precipitation of chromium hydroxide from a cold 1N solution of chromium nitrate by 1N sodium hydroxide. The precipitate was washed anion free, dried at 110°C, screened to 8-10 mesh and then heated in an atmosphere of hydrogen at a slowly increased temperature up to 500°C. Catalyst 2 was made by redissolving precipitated chromium hydroxide in excess sodium hydroxide. The chromite solution on standing over night gave a fine precipitated chromium hydroxide in

excess sodium hydroxide. Catalyst 3 was made by the ignition of chromium nitrate followed by heating in a stream of hydrogen up to 500°C. Catalyst 4 was made by precipitation of chromium hydroxide gel from a cold 0.1N chromium nitrate solution by 0.1N ammonium hydroxide. The precipitate was washed and dried as with catalysts 1 and 2. The relative dehydrocyclisation activity, as determined by conversion of n-heptane to toluene, was found to be 100%, 7%, 7% and 100%. While the first three catalysts were found to have the same activity for diethyl ketone formation from n-propanol, the fourth preparation was inactive. No dehydration of alcohol was reported. Later work[5] showed that presence of sodium in the catalyst has a beneficial effect, the optimum sodium content being 1%.

Use of alumina support for chromia

Most commercial catalysts consist primarily of one or more active constituents based or supported on an 'inert' material called catalyst carrier or support. The desirable effects which a support imparts to the catalyst may be one or more of the following:-

1. Giving a larger exposed surface of active agent and thereby greater catalytic activity per unit weight in cases where this agent by itself has a low surface area.

2. Increasing catalyst stability by keeping fine crystals of the active constituent too far apart for sintering to occur.

3. Favourably modifying the catalytic activity or selectivity, poison resistance etc., of the active constituent.

4. Helping to dissipate heat and prevent local over-heating which would cause sintering with resultant loss of active surface.

5. Imparting mechanical strength to the catalyst. This is particularly important in industrial operations from the point of view of material handling. In operations involving large heat effects a fluidized bed is very desirable for which attrition resistance is required.

6. Physical structure has been found to have important effect on selectivity.

7. The increase of active surface resulting from use of a carrier may result in a decrease in sensitivity to poisons.

In many cases catalyst support in addition to acting as a mechanical support for the active component also catalyses one of the steps of the reaction thereby acting as a promoter or co-catalyst. However it is necessary that the support chosen, by itself or due to any modifying action of the active component does not result in any undesirable side reactions for the particular

system. There is enough evidence in the literature to show that supporting chromia on γ-alumina increases the active life of the catalyst probably by preventing any sintering of chromia and that a better dispersion of active component leading to greater catalytic activity can be achieved. Thus in connection with his work on dehydrogenation of gaseous paraffins, Grosse[10] reports that pure chromic oxide is not suitable as a catalyst above 450 - 500°C; it rapidly loses its activity as a result of crystallization of the amorphous oxide. The deposition of the chromic oxide on major portions of γ-alumina allows the preparation of a stable and very active catalyst. However any other suitable material with a stable surface may be substituted for γ-alumina.

A large amount of work has been done on the catalytic conversion of n-heptane to toluene using chromia-alumina catalyst. Grosse[11] reports that pure Cr_2O_3 while found to produce partial cyclisation at 450 - 500°C was found to rapidly lose activity at higher temperatures as a result of crystallization. Introduction of suitable carrier allows the preparation of active catalysts with a useful life of over 1000 hours. Support used was Grade A activated alumina of Aluminum Corporation of America. Archibald[1] found γ-alumina to be a better catalyst support than α-alumina for converting n-heptane to toluene with chromia-alumina catalyst. However no reaction of n-heptane on

either support was detected.

Selwood and coworkers[6] have studied the applicability of magnetic measurements to catalysts with a view to investigate the effective dispersion of an active component on a support. A number of catalyst preparations of chromium content varying from 0.1 to 40% were prepared by impregnation of high surface area γ-alumina with chromic acid solutions followed by drying, ignition and reduction with hydrogen. The reduced catalysts did not have any chromium in higher oxidation state. A close relationship between magnetic susceptibility and catalytic activity, for dehydrocyclisation of n-heptane to toluene, as a function of chromium concentration was observed. This is believed to indicate that magnetic susceptibility is related to dispersion of the catalyst which in turn influences the catalytic activity. Magnetic measurements have shown that effective dispersion progressively decreases with increase in chromium content. It is generally expected that in impregnation catalysts the active component will form a uniform monomolecular layer on the support and when the active component concentration increases beyond that corresponding to monomolecular layer a second layer is formed and so on. Russell[21] studied the activity of molybdenum oxide deposited on alumina and found that the activity increased with increasing molybdenum concentration until a

monolayer is formed after which the activity stays constant indicating that molybdenum oxide does cover the whole alumina surface and a monolayer is enough for full catalyst activity. As against this Selwood[6] showed that at 6% chromium content, which is not enough to form a monomolecular layer of chromia on high area alumina used, the small portion of alumina covered has chromia in the form of very small, widely scattered, micro-crystalline particles and that there are large areas of alumina exposed between the spots.

Selwood and coworkers[22] carried out magnetic measurements on a number of miscellaneous preparations to obtain more information on chromia-alumina catalyst system. As a result of the nature of distribution of chromia nuclei, it was expected that an increase in impregnation temperature would reduce the size of the crystallites and modify the distribution of chromia. Comparison of results obtained by impregnation at room temperature and at 90°C indicated that chromium is about twice as effectively dispersed by hot impregnation as by cold. Influence of surface area of support was studied by using three different supports - γ-alumina with surface area 290 sq. m/gm.; bohemite with surface area 170 sq. m/gm and α-alumina with surface area 5 sq. m/gm. From magnetic susceptibility studies it was concluded that gross changes in carrier area have a large effect

on the dispersion of chromia provided that measurements are being made in a region where most of the surface is covered. Influence of heating the catalyst was studied by heating a 7% chromium impregnated on γ-alumina for two weeks at 600°C in air and then reducing with hydrogen. There was certainly no evidence that loss of activity is caused by an aggregation or growth of chromia microcrystals. Studies on precipitated catalyst obtained by precipitating chromia on γ-alumina showed that chromia particles varied in size from substantially isolated chromium ions to macrocrystals as compared to a fairly uniform atomic environment in impregnation catalysts. X-ray examination showed that most intense diffraction line for Cr_2O_3 appears at chromium concentrations in excess of 30% in impregnation series, down to about 10% in precipitation series, down to less than 5% chromium for chromia supported by impregnation on low surface area α-alumina and at less than 1% for a mechanical mixture of crystalline Cr_2O_3 and γ-alumina. In coprecipitation series the degree of dispersion of 35% chromium sample was the same as for 7% chromium in impregnation series. This is attributed to a three dimensional dispersion in coprecipitation series as compared to two dimensional dispersion in impregnation series. However a three dimensional dispersion does not necessarily mean a more effective catalyst preparation.

Voltz and Weller[26] investigated the relationship between electrical and catalytic properties of chromia and chromia-alumina catalysts by changing the properties of the catalysts by pretreatment. The chromia catalyst obtained by precipitation of chromium nitrate with ammonium hydroxide had a surface area of 124 sq. m/gm and was completely amorphous. The chromia-alumina catalyst studied contained 20% chromia supported on γ-alumina; its surface area was 50 sq. m/gm. This is standard Houdry Type R catalyst used commercially for butadiene production. Attempts to study the activity of the pretreated (reduced or oxidized) catalysts for cyclohexane dehydrogenation met with little success as it was found that at operating temperatures (450 - 500°C) the catalyst was brought to the same conditions of conductivity and activity as soon as the reaction started regardless of its pretreatment. Hydrogen - deutrium exchange reaction was selected for activity studies as this reaction can be carried out at low enough temperatures where catalyst pretreatment is not nullified. Chromia catalyst was cycled in hydrogen and oxygen at 500°C till a steady condition of composition and area was reached. Area of the cycled catalyst was 14-35 sq. m/gm. The colour of the catalyst was black-dark green in oxidized state and bright green in the reduced state. X-ray diffraction pattern showed the presence of very small crystallites of α-chromia in the cycled catalyst. The

reduced form was much more active than the oxidized form. Freshly prepared reduced catalyst is reported to be more active than the cycled one. This is attributed to a five-fold decrease in surface area which occurs on cycling. Chromia-alumina catalyst was also found to be more active in the reduced state than in the oxidized one though the difference is not as much as with chromia alone. The results indicate a stabilization of trivalent chromium by the alumina support and that chromia is three times more effectively distributed in the supported than in the unsupported catalyst.

During the last twenty-five years a very large amount of work had been done to correlate the electrical properties and catalytic activity of various catalysts. Garner[7] reports that Dowden has studied the electrical changes that occur during the reaction of isopropyl alcohol on chromia-alumina, magnesia-alumina and zinc oxide-alumina. It was shown that dehydrogenation is favoured with n-type conductors (excess ZnO) and dehydration by substances normally described as p-type oxides (e.g., Cr_2O_3).

Griffith and coworkers [3,4,9] have published a series of papers on their studies on coprecipitated chromia-alumina catalysts. They studied surface areas, adsorption characteristics, electrical conductivity, ring closing activity and kinetics, structure by x-ray diffraction and magnetic susceptibility. They

showed that catalysts reduced in hydrogen at 500°C are n-type semi-conductors if they contain more than about 35% of chromium oxide; those with lower chromium content and all mixtures after heating in air are p-type semi-conductors. Carbonaceous deposit on the catalyst was observed. By comparing Dowden's and Griffith's work it is apparent that depending on the preparation method chromia catalyst may either be a dehydrogenating or a dehydrating catalyst. This picture may explain the observations of Sabatier[19] and Lazier et al[19].

The information on the activity of alumina itself is very contradictory. In addition to its extensive use as a catalyst support alumina is widely used as a catalyst or co-catalyst for dehydration, hydration, isomerization, catalytic cracking, etc. In spite of the extensive use of alumina the literature reveals striking discrepencies with respect to its catalytic activity. To cite a few examples[20] the dehydration of primary alcohols such as 1-butanol is reported by many authors to give pure 1-olefin whereas others found mixtures of double bond isomers. Further some workers report that olefins undergo only double bond shift without skeletal rearrangement over alumina while others have observed skeletal rearrangement. Tollefson[25] studied the catalytic dehydrogenation of n-propanol using zinc oxide on alumina and obtained only minor amounts of propylene; up to 3%

in gaseous products. Hansen[12] studied the same reaction using chromia on alumina and obtained from 20 to 45% propylene in the gaseous products. Tollefson and Hansen used the same alumina support. Komarewsky and Coley[16] obtained simultaneous dehydration-dehydrogenation of C_6 to C_8 normal aliphatic alcohols using coprecipitated chromia-alumina catalyst. They attributed dehydration to alumina and dehydrogenation to chromia. At least one industrial process[24] uses zinc oxide on alumina for production of methyl ethyl ketone from secondary butanol without getting any dehydration. As against this alumina is generally regarded as a good dehydration catalyst for alcohols.

This contradictory picture leads to the fact that not all alumina preparations are similar with respect to catalytic activity. A series of distinct phases with different crystal structures are known to exist. The method of preparation and pretreatment influence the crystal structure of alumina and inclusion of any impurities which in turn influence its catalytic activity.

Stumpf et al[23] have studied the thermal transformations of aluminas and aluminum hydrates. Seven crystalline modifications of the nearly anhydrous aluminas obtained by heating pure alumina hydrates were called α-, γ-, δ-, η-, κ-, θ-, and χ-alumina. Four hydrates namely α- and β-trihydrate

and α- and β-monohydrate were studied. The basic sequences of transformations occurring in dry air or steam when the alumina hydrates are heated to successively higher temperatures are

α-trihydrate goes to α-monohydrate to χ-, to γ-, to κ-, to θ-, to α-alumina.

β-trihydrate goes to α-monohydrate, to η-, to θ-, to α-alumina.

α-monohydrate goes to γ-, to δ-, to θ-, to α-alumina.

β-monohydrate goes to α-alumina.

The transformation temperatures depend upon time of heating, atmosphere, hydrate particle size and purity.

Winfield[28] reports that while consensus of opinion is that γ-alumina is catalytically active for dehydration its nature cannot be regarded as settled beyond doubt.

Method of preparation affects the activity of alumina. Senderens[28] prepared alumina by decomposing aluminum sulfate at red heat. Later he precipitated aluminum hydroxide from a solution of sodium aluminate treated with dilute sulfuric acid. It was washed a number of times with cold and then with boiling water and finally dried at a low temperature. The latter of the two preparations had higher activity for dehydration and lower

activity for dehydrogenation. Increasing thoroughness of washing was shown to increase the dehydrating activity of the final product. Clark et al[28] claimed absolute purity of the catalyst to be essential for good dehydration. Alkali is repeatedly mentioned in literature as an inhibitor for dehydration. de Boer[28] prepared alumina via aluminum propoxide so as to avoid any contamination with foreign ions and obtained what he called 'perfectly neutral alumina'.

Recently Pines and coworkers[20] have done extensive investigations on use of alumina as catalyst and support. They report that there is enough evidence to show that pure alumina has intrinsic acidity. Thus the reactions catalysed by alumina are typically acid catalysed such as dehydration of alcohols and skeletal isomerization of 3.3-dimethyl butene and cyclohexene. The various test methods were found to give the same picture of the acidity for certain aluminas but not for all. Thus alcohol dehydration is considered primarily a function of the number of acid sites and can be caused by relatively weak acids. On the other hand isomerization of cyclohexene occurs only on acid sites of considerable strength. Pure alumina from aluminum isopropoxide or from nitrate and ammonia and calcined at 700°C showed optimum activity on a weight and on a unit surface area basis. Heating at higher temperatures decreased the number of

acid sites as well as their acid strength. Impregnation of pure alumina with either sodium hydroxide or sodium chloride was shown to lead to a partial poisoning of the active sites without appreciably changing the acid strength of the remaining sites. With increasing amount of alkali there is a parallel decrease in the activity for cyclohexene conversion and for butanol dehydration. Aluminas from sodium or potassium aluminate contain alkali in an amount which depends on the way of precipitation and number of washings. Samples with 0.08 - 0.65% sodium were found to have a large amount of weakly acid sites but no strong acid sites. As such they are claimed to be excellent dehydration catalyst and would not result in any isomerization of cyclohexene.

Gremillion[8] reports that Bridges et al have concluded from their work on chromia-alumina catalyst that acid sites on bare alumina are responsible for formation of species which poison dehydrogenation sites on the chromia surface.

It is clear that no definite conclusions regarding the best method of chromia catalyst preparation can be reached from the available literature. However the following general observations may be made and a catalyst may be prepared in light of these.

1. Chromia catalysts of widely varying activity may be obtained depending on the method of preparation and pretreatment.

2. A particular chromia preparation may be active only for a specific reaction while another chromia preparation may be required for another reaction.

3. Certain chromia catalysts have a moderate activity for converting n-propanol to diethyl ketone.

4. Chromia catalyst is active in amorphous form and may lose activity with time. Active life can in general be extended by using γ-alumina as support.

5. Of the supported catalysts the impregnation type seem to be better than coprecipitation type.

6. High surface area supports result in better dispersion of active component. In case of chromia-alumina effective dispersion decreases with increase in chromium concentration.

7. Reduced catalyst may be more active than the oxidized form except when reaction conditions may even out any pretreatment.

8. Certain alumina preparations are very active dehydration catalysts and may introduce undesirable side reactions.

9. Acid sites on active alumina are responsible for dehydrating and isomerization activity of alumina. Any method that results in loss of acid sites decreases the activity of alumina; one commonly reported method is to add sodium to the alumina.

III - CATALYST PREPARATION

The physical and chemical properties that determine the activity and selectivity of a catalyst for a specific reaction depend on the total history of catalyst preparation. In order that the variation in catalyst properties and hence activity and selectivity in successive preparations be reduced to a minimum it is necessary that an exact and detailed method of preparation be available. The fact that every minor detail may have a profound influence on catalyst activity can hardly be over emphasized.

Originally the catalyst selected for study was chromia based on γ-alumina obtained by the impregnation of intermediate surface area γ-alumina with chromium nitrate solution followed by drying and decomposing the salt at high temperature. Later work showed that this catalyst as such was not suitable for the desired reaction as it resulted in a very substantial dehydration of n-propanol. It was considered desirable to try some additive for this catalyst that would suppress dehydration. Since the dehydration was due to alumina, as shown by runs with bare support, which is generally believed to be due to acid centres it was planned to incorporate sodium on the catalyst. Thus two catalysts were prepared; namely chromia on γ-alumina and sodium promoted chromia on γ-alumina. The detailed methods of preparation are described below:

Materials:-

1. Chromium nitrate, B.D.H. reagent grade, chemical formula $Cr(NO_3)_3 \cdot 9H_2O$.
2. Alundum catalyst carrier supplied by Norton Company. Particle size was 1/8 inch x 1/8 inch cylinders and manufacturer's specifications gave

   surface area = 60 - 70 sq. m/gm

   porosity = 60 - 65%

   water absorption = 51 - 56%

   X-ray diffraction analysis was reported to have shown predominantly γ-alumina with some α-alumina and quartz.
3. Sodium hydroxide supplied by Mallincrkodt Chemical Company, analytical reagent grade, chemical formula NaOH.

General considerations:-

Impregnation method for preparing supported catalysts is based on the fact that when a porous support is immersed in a solution of the salt, which is the desired active component or gives the desired component on further treatment, some solution is taken up by the pores of the support. When the wet solid after drainage of excess solution is dried the active component stays on the support giving the desired catalyst. In some cases the dried material has to be treated further to get the desired

catalyst. The amount of active component deposited depends on the porosity of the support and the concentration of the solution. In other words, with a support of given porosity, the concentration of the impregnating solution depends on the desired concentration of active component in the catalyst.

Active component concentration may be fixed on the basis of any available literature information, experience or in an arbitrary way. Selwood concluded that optimum concentration of chromia on γ-alumina is reached at a concentration below that required to cover the entire support surface area with a monomolecular layer of the active component. Thus the concentration required to cover the support surface area with a monomolecular layer of the active component gives the upper limit. According to Innes[13], if the catalytic agent deposits as a monomolecular layer, the amount necessary to cover the surface can be estimated from the expression

$$\frac{\text{Weight of catalytic agent}}{\text{Weight of carrier}} = \frac{S \cdot d^{2/3} \cdot M^{1/3} \cdot 10^4}{N^{1/3}}$$

where S is specific area of carrier in sq. m/gm

M is molecular weight of catalytic agent

d is density of catalytic agent

N is Avogadro's number

Taking S = 70 and d = 2.35 we get:

$$\frac{\text{Weight of } Cr_2O_3}{\text{gm. of support}} = 0.0784 \text{ gm.}$$

$$= 8\% \text{ (approximately)}$$

Chromia on γ-alumina catalyst:-

To prepare a catalyst containing 8% Cr_2O_3 on a given support one needs the porosity of the support. Porosity as determined by the helium mercury method is not suitable for this purpose because under the conditions of impregnation not all the pore space in the support is filled up by the solution. The amount of pore space actually filled up depends on the nature of solution, temperature and time of impregnation. Thus porosity as determined by helium mercury method is more than that determined by using water. While an exact value must be determined by using the actual solution to be used for impregnation a preliminary idea may be obtained by finding out the amount of water taken up by a definite weight of support. With the support used it was found that 50.6 gms. of water were taken up by 100 gms of support when absorption of water was allowed to take place at room temperature for one hour in presence of large excess of water. Using the same figure (50.6%) for chromic nitrate solution it can be calculated that to get 8% Cr_2O_3 in the catalyst the concentration of the solution should be 15.8% Cr_2O_3. When using 15.8% Cr_2O_3 solution

the absorption of this solution was found to be less than that of water. After a few trials it was found that a 21% Cr_2O_3 solution would give 8.8% Cr_2O_3 in the support. Chemical analysis of the catalyst obtained by using 15.8% chromia solution showed that actual Cr_2O_3 content of the final catalyst was less than that calculated. Keeping this in view, it was considered desirable to use a 21% Cr_2O_3 solution for preparing approximately 8% Cr_2O_3 catalyst.

Experimental method:-

A 21% Cr_2O_3 solution was obtained by dissolving 310 gms of B.D.H. reagent grade chromic nitrate in 100 cc of distilled water. The solution obtained had a density of 1.45 and was deep blue in colour. 250 gms. of catalyst support was immersed in 250 cc of this solution in a large beaker. The volume of solution taken was about 2-1/2 times that required to fill the pores. After intermittent stirring of the whole mass for one hour the excess solution was drained out. The colour of the wet solids was light blue. The drained solids were dried in an air oven at 100 $\pm$5°C for 10 hours. Drying at room temperature was found to be unsuitable as chromium salt was found to crystallize out as loose particles on the surface when wet solids were left to dry at room temperature. As against this the solids dried at 100 $\pm$5°C had no salt crystallized as large sized particles on their

surface and appeared to the naked eye to have a uniform texture. The colour of the apparently dried material was light green and it smelled of oxides of nitrogen due to some decomposition of the nitrate which sets in at drying temperatures. The solids were then decomposed in a furnace in the presence of air. The temperature of the furnace was raised to 350°C in 1-1/2 hours and the heating continued at 350°C for 4 hours. The catalyst obtained was light brown in colour with a few dark particles.

For experimental work another sample of catalyst starting with 1000 gms. of catalyst support was prepared by the same procedure.

Sodium promoted chromia on γ-alumina catalyst:-

It was arbitrarily decided to incorporate 3% sodium by weight on the previously prepared chromia on γ-alumina catalyst. Preliminary calculations similar to those carried out for first catalyst showed that 13% NaOH solution was required for sodium impregnation. Since chromia in oxidized state is soluble in sodium hydroxide solution it was necessary to reduce the catalyst before impregnating sodium. Runs 6 and 7 had shown that during the course of reaction chromia was reduced by the hydrogen produced. As such the catalyst charge removed from the reactor after run number 7 was used for sodium impregnation.

Experimental procedure:-

400 gms of chromia on γ-alumina catalyst was immersed in 400 cc of 13% NaOH solution. After 1 hour of intermittent stirring the excess sodium hydroxide solution was drained. The solution retained by the solids was 160 cc. The drained solids were dried at $105 \pm 5°C$ for 6 hours and the weight of dried solids was found to be 417.5 gms.

IV - EXPERIMENTAL EQUIPMENT

A fluidized bed equipment as used by Hansen[12] for his studies on dehydrogenation of n-propanol and propionaldehyde with a chromia catalyst was available for use. It was decided to explore the suitability of this equipment for present studies in a fixed bed. Another object of using this equipment was to get some information for the design of better equipment for further studies on the same system. The original equipment along with the changes made for this study is described below. A schematic diagram and a photograph of the equipment are included in Figure 1 and Plate 1 respectively.

Reactor

Figure 2 is the detailed diagram of the reactor. The original fluidized bed reactor was constructed of type 316 stainless steel except for the low carbon steel flanges. A 4 foot section of 2-inch standard pipe was used as the main reactor section enlarging into a 2 foot section of 4-inch diameter disengaging zone provided with a baffle plate and porous stainless steel filter to eliminate carryover of the catalyst into the condensing system. The catalyst support grid plate consisted of a circular section of 1/8-inch porous stainless

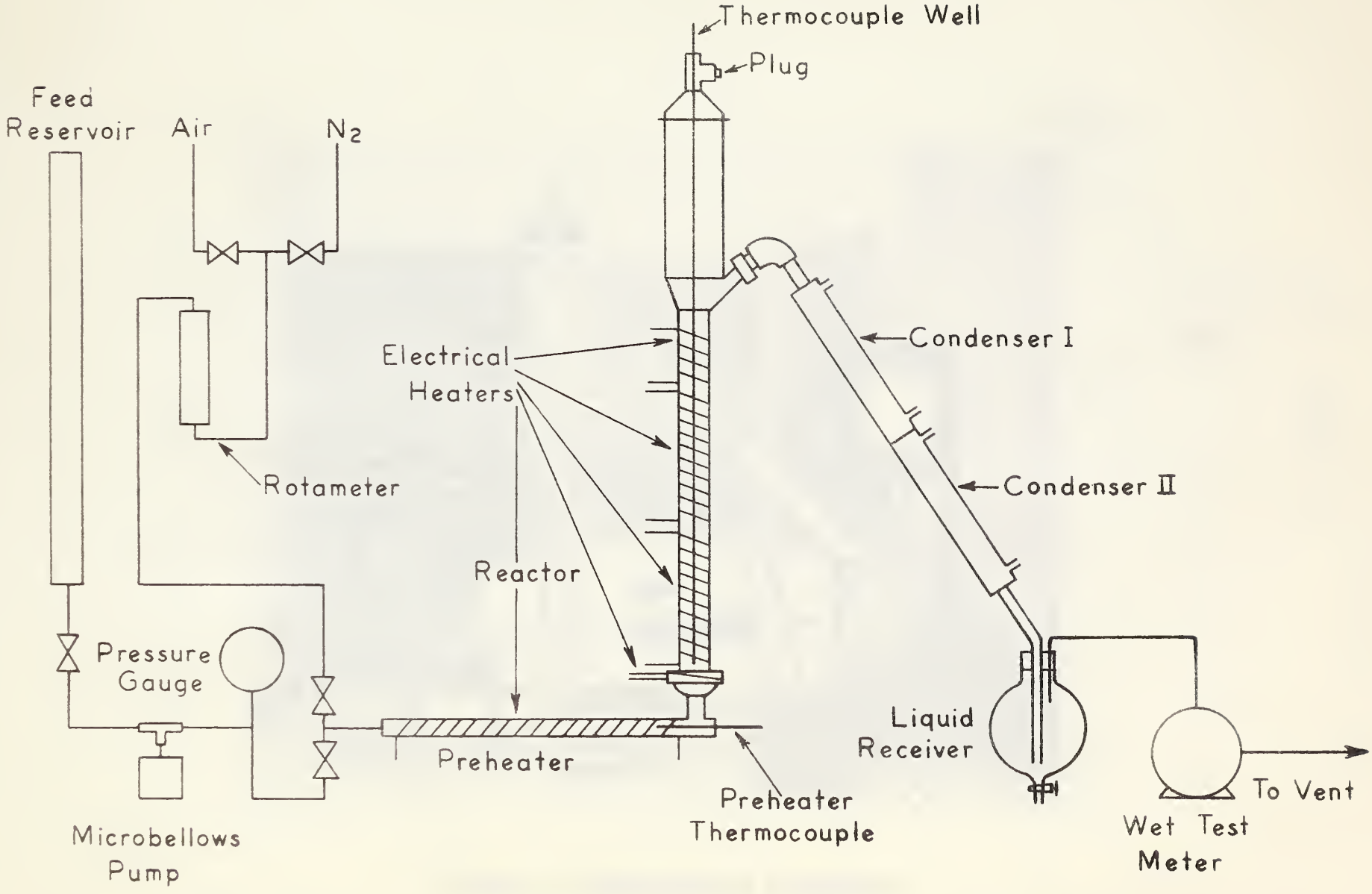


FIGURE 1 - SCHEMATIC APPARATUS ASSEMBLY

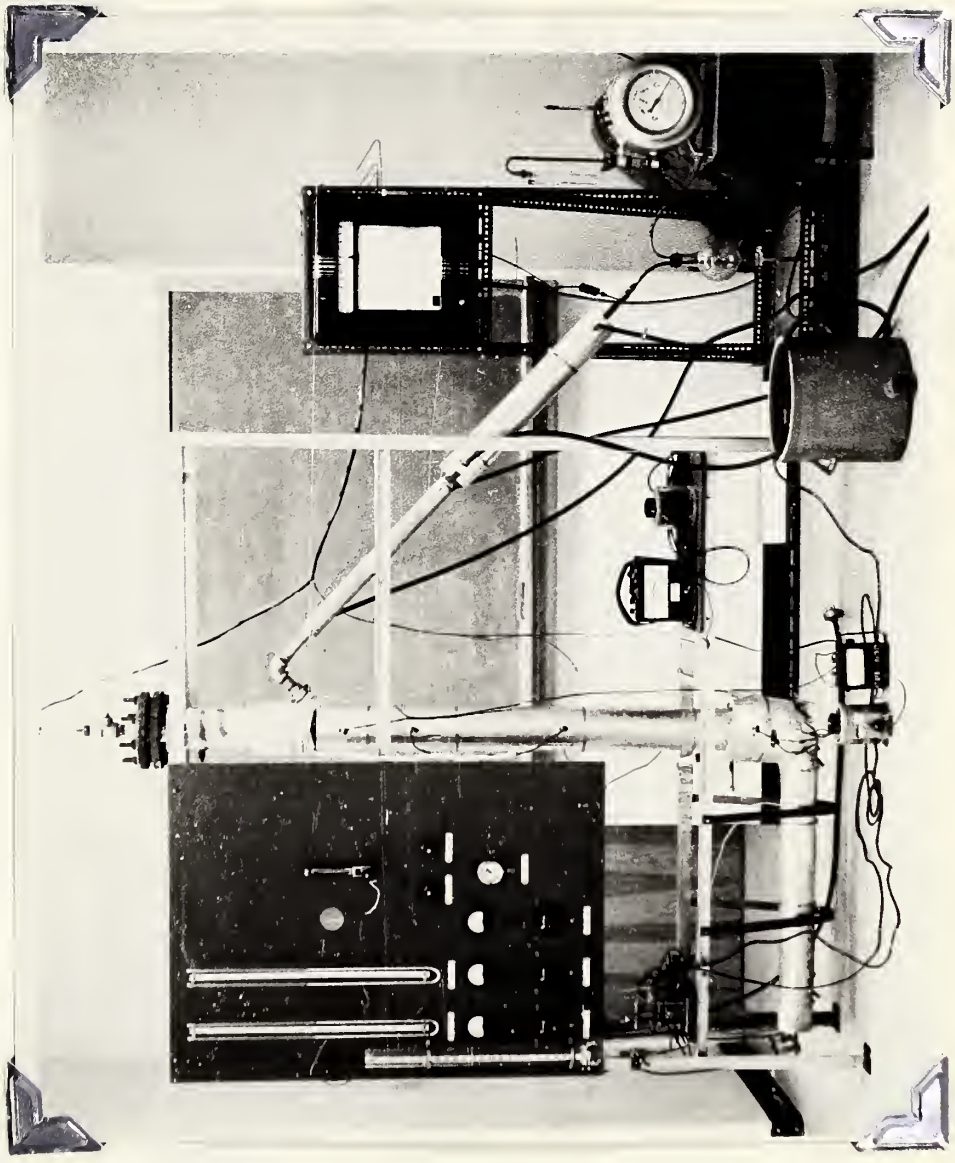


PLATE 1 - EXPERIMENTAL EQUIPMENT

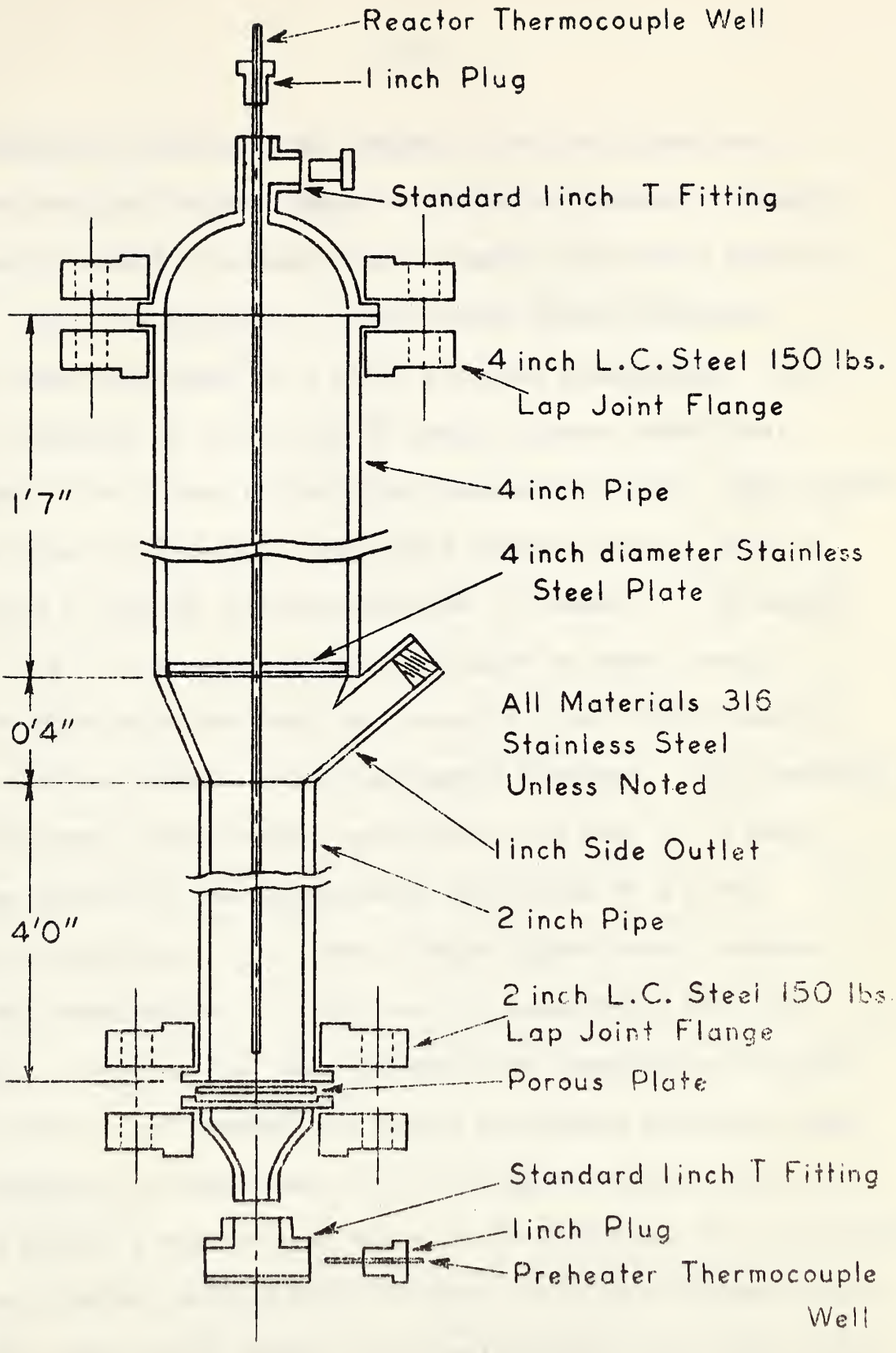


FIGURE 2 - DETAILED DIAGRAM OF REACTOR

steel supplied by Micrometals Company. The grid plate was recessed into the bottom flange in the lower reactor. Pressure taps were provided to measure the pressure drop across the bed.

Heat was supplied to the reactor by two 1000-watt heaters each controlled by a 1 KVA variable transformer. Each heater consisted of 20 feet of 20 gauge nichrome electrical resistance wire strung on porcelain insulating beads. Each heater covered about 20 inches of the 4 foot section and was held in place with a coating of Saurereisen No. 29 cement. A 10 ampere ammeter and a 10 ampere fuse were included in each circuit. Asbestos insulation was used as a cover for the 2-inch reactor section and was sheathed with corrugated aluminum. The disengaging zone and upper flange heater consisted of 18 feet of 20 gauge nichrome electrical resistance wire controlled by a 1 KVA variable transformer. The lower flange fitted onto a reducer which was connected to a 1-inch tee for connections with the preheater. This part of the equipment was insulated with loose flake asbestos and covered with formed corrugated aluminum sheet. This equipment had been used with a -40 mesh catalyst charge of 1850 cc giving a settled bed height of 28.5 inches. For the present work the catalyst pellets were 1/8 inch x 1/8 inch cylinders and since the superficial linear gas velocities were low enough there was no danger of catalyst carryover. This eliminated the need for a disengaging section and in order to reduce the homogeneous reactor

volume it was decided to block off the 4-inch disengaging section. This was achieved by tight fitting a circular stainless steel plate in the lower end of disengaging zone. An outlet for the product vapors was provided at the tapered section between 2-inch and 4-inch sections.

Preheater

A 3 foot section of 1-inch schedule 40 stainless steel pipe was threaded into the side outlet of a tee at the lower end of the reactor. Liquid alcohol was admitted through a 1/4 inch O.D. stainless steel tube silver soldered into a 1-inch stainless steel cap threaded to the 1-inch pipe. A 20 foot, 20 gauge nichrome electrical resistance heater constructed and controlled similarly to the reactor heaters supplied heat required to vaporize the liquid alcohol and heat the vapors to the desired level of temperature. Asbestos insulation sheathed with corrugated aluminum was used as preheater insulation.

Condensing system

Two condensers of identical construction were used to condense the hot gaseous products from the reactor. Each condenser was constructed by placing a nine tube bundle in a 2 foot, 2-inch

I.D. copper shell. The tube bundle consisted of 1/4-inch copper tubing. The first condenser was cooled with water at room temperature while the second one placed immediately next to the first was cooled with ice-cold water recirculated through it with a pump. The outlet from the final condenser led into a liquid product receiver from where the uncondensed gases passed to an oil filled test meter. The liquid product could be drained from the receiver as and when required. The gaseous product was vented, after being measured,except when a sample for analysis was collected over mercury in a gas burette.

Alcohol feed system

A calibrated glass tube, 2 inches in diameter and 24 inches long served as a feed reservoir for a Research Appliances Model 1000 stainless steel, 3/4 inch microbellows positive displacement pump. The discharge line of the pump led to a needle valve located close to the preheater inlet. The feed rate could be adjusted by an adjustment nut provided on the pump to adjust the expansion of the bellows and hence the liquid flow rate. In addition, a needle valve between reservoir and the pump was used to manually control the feed rate. In practice it was found possible to keep the feed rate constant.

Air and nitrogen supply system

Arrangements were provided to supply air for oxidizing the catalyst before every run and nitrogen for purging the system before starting the alcohol feed for the run. The gas line led to the preheater through a needle valve located close to the preheater inlet and parallel to the needle valve for alcohol feed. A calibrated rotameter was located in the line to measure the gas flow rate.

Temperature measurements

A single iron-constantan thermocouple was installed to measure vapor temperature in the preheater. A two-hole ceramic insulator fitted into a 1/8 inch I.D. thin wall stainless steel tube supported the wires. The tube was silver soldered into a standard stainless steel 1 inch plug extending the thermocouple junction 6 inches into the preheater when threaded into the lower reactor tee fitting. The protruding end of the supporting tube was insulated with 1/8 inch asbestos string.

Temperature measurement in the reactor was accomplished by positioning an 8 point thermocouple string from the upper tee fitting of the reactor to within 1 inch of the grid plate. A common constantan wire extended to the lowest point of the thermo-

couple string; the iron wires extending to the thermocouple junction points along the constantan wire at 1, 7-3/8, 13-1/2, 19-3/4, 26, 32-3/8, 44-3/4, and 63-1/4 inches from the bottom grid plate. These points were numbered 8,7,6,5,4,3,2,1 respectively i.e., thermocouple numbers 1 to 8 measure temperatures from the top to the bottom of the reactor. Thermocouple number 1 lies in the disengaging zone which had been blocked off. The thermocouple wires were insulated by using 1/8 inch O.D. 2 hole ceramic insulators. The entire string was placed in a 3/8 inch I.D. thin wall stainless steel tube which was soldered into a 1 inch stainless steel plug. The ends of the thermocouple wires were attached to a nine point junction to facilitate thermocouple disconnection during removal of the thermocouple tube from the reactor.

Generally speaking radial and longitudinal temperature gradients are considerable in fixed bed reactors as compared to fluidized beds. Thus it was considered desirable to locate one more thermocouple in the existing equipment to get an idea of the order of radial gradients. For this purpose a thermocouple similar to one in the preheater was inserted at 14-3/4" from the grid plate such that the thermocouple tip was half way between the inside wall of the reactor and the centre line of the reactor. This was numbered 9. A single cold junction was held at the ice point to provide a reference potential. All thermocouples were

connected to a Leeds and Northrup twelve point adjustable range recorder. A Leeds and Northrup portable potentiometer was connected to one recorder junction for calibration of the recorder.

V - EXPERIMENTAL TECHNIQUES

Preliminary runs

Preliminary runs were carried out to establish the range of operating conditions namely space velocity and temperature that could be investigated in this equipment, the criterion being to keep the temperature of the catalyst bed nearly constant for each run.

Initially 1000 grams of γ-alumina pellets (1/8 inch x 1/8 inch cylinders) were charged in the reactor giving a bed height of 20 inches i.e., thermocouple number 5 being in the bed. When the two heaters on the reactor section were on for 5-6 hours the longitudinal temperature gradient even without any reaction in the bed was very high, the difference in temperature at the two ends being of the order of 250°C. Thermocouple number 8 is located very close to the upper flange at the lower end of the reactor and it was difficult to raise the temperature at this point beyond 175°C. This showed the necessity of heating the flanges. This was provided by winding 11 feet of 24 gauge nichrome electrical resistance wire strung on porcelain insulating beads around the flanges. The capacity of this heater was limited by the space around which the resistance wire could be wound. The winding was held in place with a 1 inch wide asbestos tape to enable it to

be removed when the flanges were to be taken apart for catalyst removal from the bed.

Runs were then planned to investigate the activity of the catalyst support alone if any. Initial runs showed that the support was very active by itself and resulted in appreciable dehydration of n-propanol. Since dehydration and dehydrogenation are both endothermic reactions, though with different heat effects, it was considered that control of reaction bed temperature would pose similar problems in the two cases. The endothermic nature of the reaction put a limit on the n-propanol feed rate so as to balance the heat taken up by the reaction to that transferred to the catalyst bed by the heaters. It was found that even at the highest alcohol feed rate for which temperatures at points 7 and 8 could be maintained nearly constant most of the reaction took place in the lower section of the bed. Since a single heater covered the lower 20 inches of the reactor the heat input required to maintain points 7 and 8 at constant temperature increased the temperature at points 5 and 6. In view of this it was decided to reduce the bed height to 8 inches so that thermocouple numbers 7 and 8 were at the two ends of the catalyst bed. The original two heaters of the 2-inch reactor section covered the lower 40 inches of the 4 foot section i.e., the section around thermocouple number 2 was not heated. In the

preliminary runs it was found that the temperature at point 2 remained lower than the bed temperature. To avoid any condensation and reflux of products from this section, a 6 feet section of 26 gauge nichrome resistance wire strung on porcelain insulating beads was wound around this section. This heater was insulated, connected and controlled in a manner similar to that for other heaters.

The maximum temperature at which the catalysts could be studied was found to be about 450°C; any attempts to use a higher temperature burnt out the heater at the flange section.

The maximum space velocity that could be used while simultaneously maintaining the catalyst bed temperature constant depended on the extent and nature of reactions which in turn depended on the temperature and the catalyst charged. As such this had to be determined from run to run.

It was also found that since the total volume of the unit (preheater, reactor and condensers) was so large, the time lag between the starting of the liquid feed and appearance of liquid product was between 5 and 15 minutes.

Operation of the equipment

The catalyst to be studied was charged in the reactor to give a bed height of 8 inches. The reactor and the preheater

were brought up to the desired temperature level. This required 4 to 5 hours. For runs 1 - 5 the system was then purged with N_2 for about 15 minutes. The cooling water for the two condensers was then turned on and the alcohol feed started. The needle valve on the alcohol feed line and the heaters were manipulated so as to maintain the reaction bed temperature within limits. When the temperature and alcohol feed rate had been stabilized a test run was made for about half an hour. During this period liquid feed rate was determined by the fall in the liquid level in the calibrated liquid feed reservoir and the temperatures in the equipment were recorded. The uncondensed gaseous products were released after being measured with a liquid filled gas test meter, except when a sample was collected for analysis. A gas sample was taken at the middle of the run and collected over mercury in a 100 ml gas burette. The condensed liquid product was collected at the end of the run and its volume and weight were determined before analysis.

For runs 6-10 the operating procedure was the same as above except that the catalyst was oxidized for every run before purging with nitrogen. The oxidation was accomplished by passing air at a rate of 0.1 cu. ft. per minute for about 40 minutes after the catalyst bed had been brought up to 250°C.

Analysis of products

Liquid products

Liquid compositions were determined by analysis using a Burrell Model K-2 Kromotog vapor phase chromatograph. As many minor fractions were expected in the product it was initially decided to focus attention on n-propanol and diethyl ketone as feed and product and propionaldehyde and 3-pentanol as intermediates. After trying a number of column packings and operating conditions it was found that di-n-decyl phthalate on celite, 25% by weight, gave a good separation. The column operating conditions were

column	- 2-1/2 meters, di-n-decyl phthalate on celite
column temperature	- 80°C
carrier gas flow rate	- Helium at 60 mls/min
detector current	- 150 milliamperes
detector thermostat	- 100°C

When runs were carried out with bare alumina support it was found that appreciable amounts of n-propanol were dehydrated to yield di-n-propyl ether, water and propylene. It was found possible to separate di-n-propyl ether on the same column with the operating conditions already chosen. However water content could not be found using this column because water peak tailed off giving a non-reproducible calibration curve. Further consideration showed

that since water is produced by two different reactions namely, dehydration to di-n-propyl ether and dehydration to propylene in which the ratio of water produced to n-propanol reacted is different, water analysis by itself could not have given a measure of the proportion of n-propanol dehydrated.

For quantitative analysis calibration curves giving peak heights as a function of volume or pure components were prepared for each of the components. The calibration curves are shown in Figure 3. Peak heights were preferred to peak areas for calibration because peak area versus volume did not yield a linear relation and propionaldehyde peak was too narrow for an accurate area determination. On the other hand peak height versus volume gave linear relation for two components and peak heights can be directly read without the loss of accuracy associated with peak area determination.

Quantitative determination was based on the assumption that peak height of a component is dependent only on the amount of the component and is independent of any other components in the mixture. Thus knowing the peak heights one knows the amounts of the corresponding components in the mixture and hence its composition. If the peaks obtained did not account for 100%, as was often the case, the balance was reported as 'others'. The amount of water formed was estimated by analyzing the aqueous

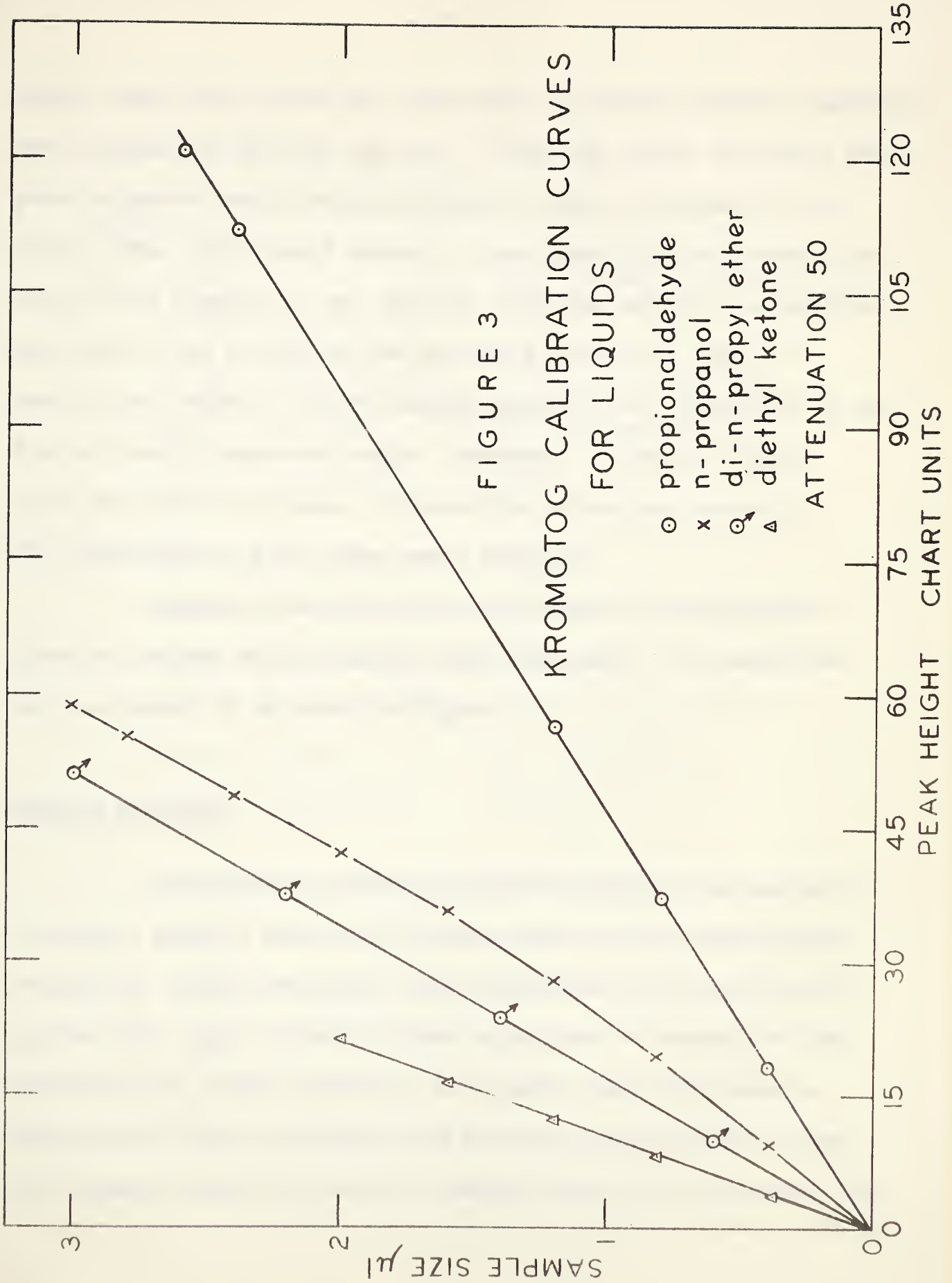


FIGURE 3
KROMOTOG CALIBRATION CURVES
FOR LIQUIDS
⊙ propionaldehyde
× n-propanol
⊙ di-n-propyl ether
△ diethyl ketone
ATTENUATION 50
PEAK HEIGHT CHART UNITS
0
15
30
45
60
75
90
105
120
135
SAMPLE SIZE μl
0
1
2
3

layer, when such a layer was separated, for known organic components and considering the rest as water. With the column used only five peaks appeared namely propionaldehyde, water, n-propanol, di-n-propyl ether and diethyl ketone. Since these did not account for 100% of the mixture it was apparent that the rest of the material was held in the column at the operating conditions used. On heating the column to 120°C unknown material was driven out in the form of poorly separated peaks. Attempts to identify these peaks met with no success. However the column was heated to 120°C for about 1 hour after every analysis.

Component identification was based on the retention times as checked with those for pure components. Chromatogram for run number 10 is shown in Figure 5.

Gaseous products

Quantitative analysis of gaseous product was carried out by using a Burrell Model K-2 Kromotog vapor phase chromatograph as used for liquid analysis. The product was to be analyzed for H_2, CO, CO_2, C_3H_6, N_2 and O_2; the latter two to correct for any contamination while sampling. No single column was found to separate all these components and as such it was decided to use two columns; molecular sieve for separating H_2, O_2, N_2 and CO and

silica gel for CO_2 and C_3H_6. The column operating conditions are given below:-

Column No. 1

column	-	2-1/2 meters, molecular sieve 13X
column temperature	-	50°C
carrier gas flow rate	-	Helium at 82 mls/min
detector current	-	220 milliamperes
detector thermostat	-	100°C

Column No. 2

column	-	2-1/2 meters, silica gel
column temperature	-	80°C
carrier gas flow rate	-	Helium at 90 mls/min
detector current	-	170 milliamperes
detector thermostat	-	100°C

Quantitative determination was carried out by the same method as used for liquid products. Calibration curves giving peak height as a function of volume of the compound were prepared for each of the components (See Figure 4). For this a number of gas samplers of different volumes were prepared and their volumes determined from the weights of mercury required to fill them. Hydrogen was found to show an abnormal behaviour in that when the

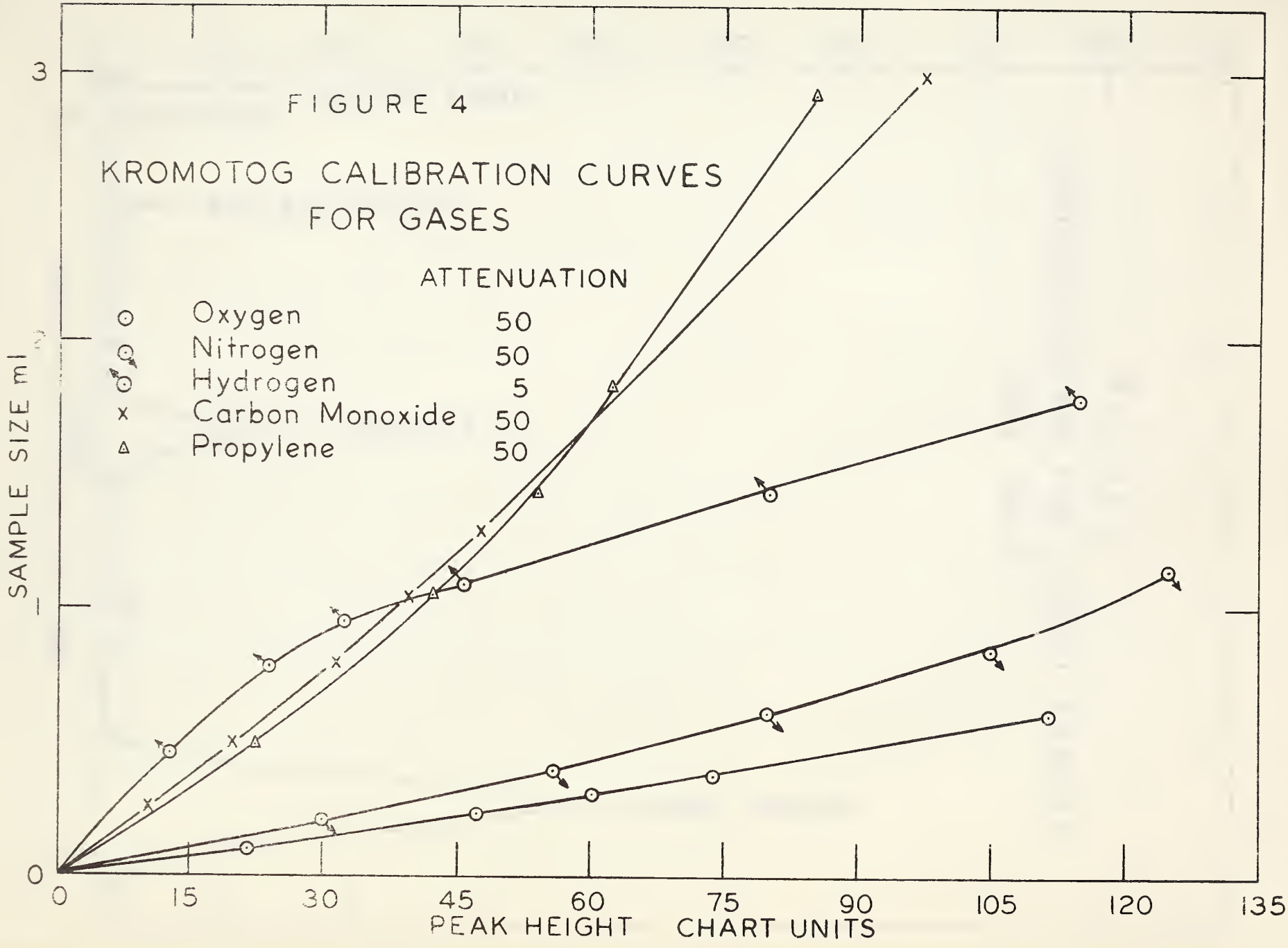
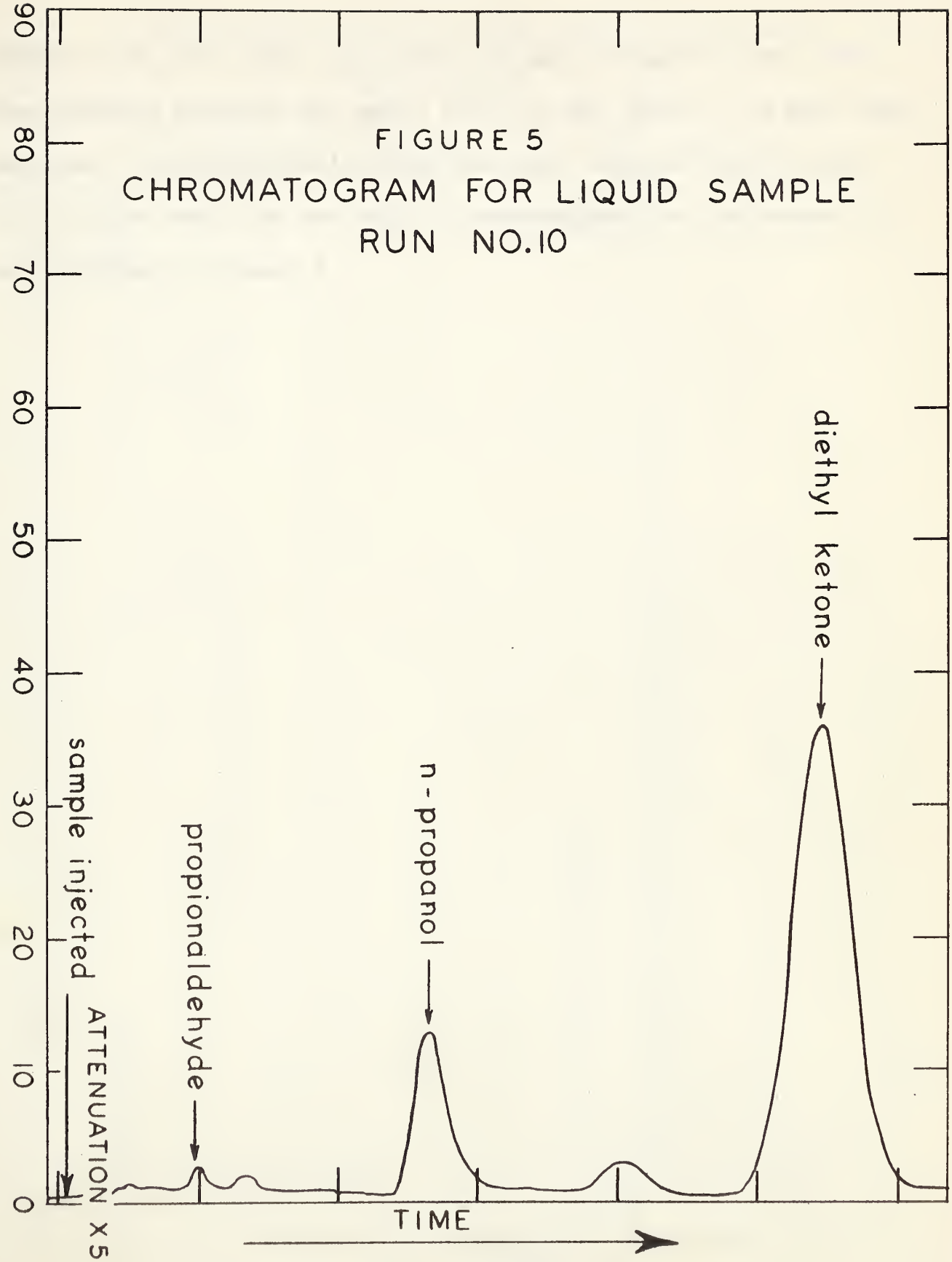


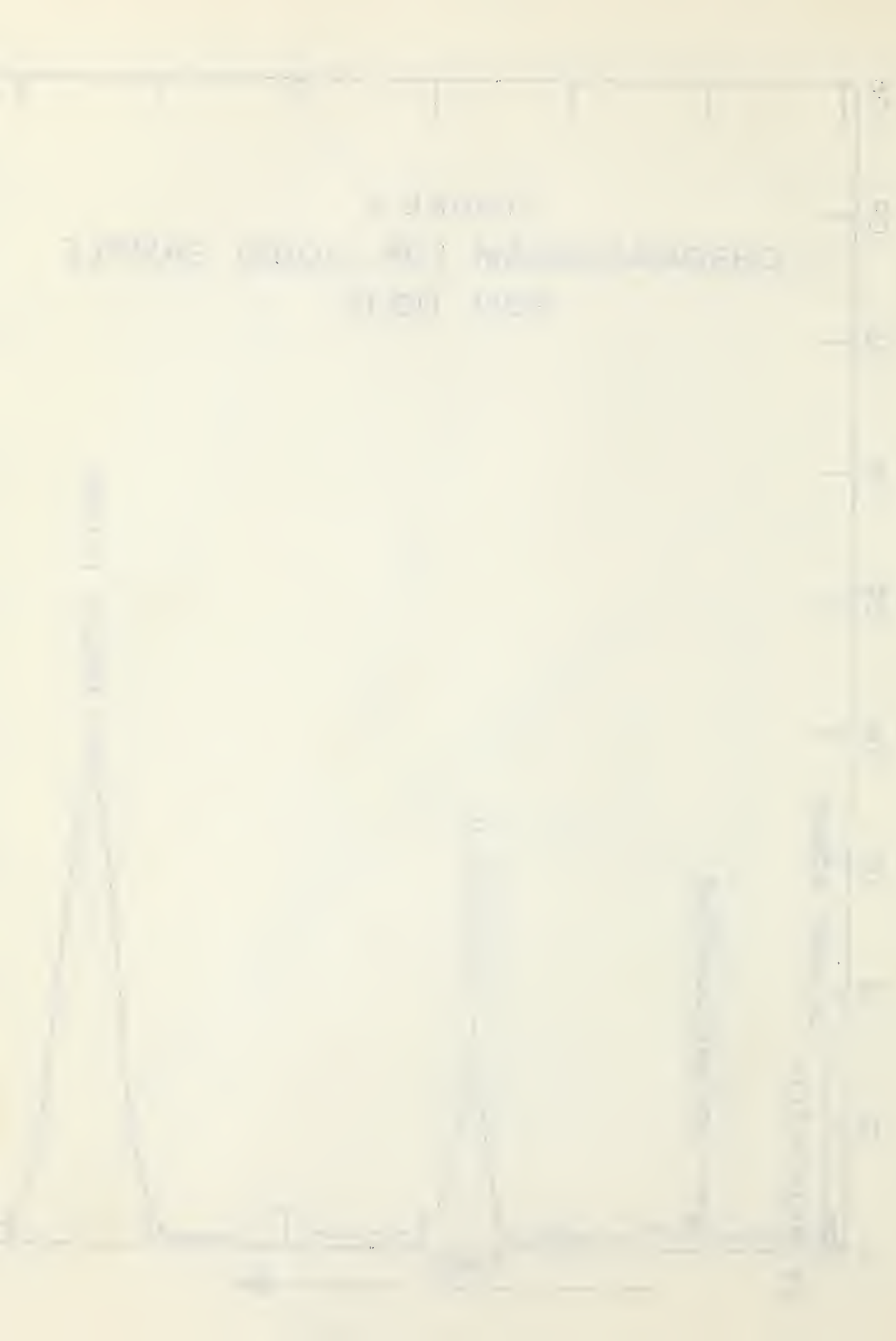
FIGURE 4
KROMOTOG CALIBRATION CURVES
FOR GASES
ATTENUATION
Oxygen 50
Nitrogen 50
Hydrogen 5
Carbon Monoxide 50
Propylene 50
SAMPLE SIZE ml
3
0
0
15
30
45
60
75
90
105
120
135
PEAK HEIGHT CHART UNITS

FIGURE 5

CHROMATOGRAM FOR LIQUID SAMPLE

RUN NO.10





amount of H_2 was large in a sample it gave a negative peak i.e., the Kromotog recorder pen moved first to the left of the base line and then to the right well below the base line and again to the left of the base line and back. Chromatograms for run number 10 are included in Figure 6.

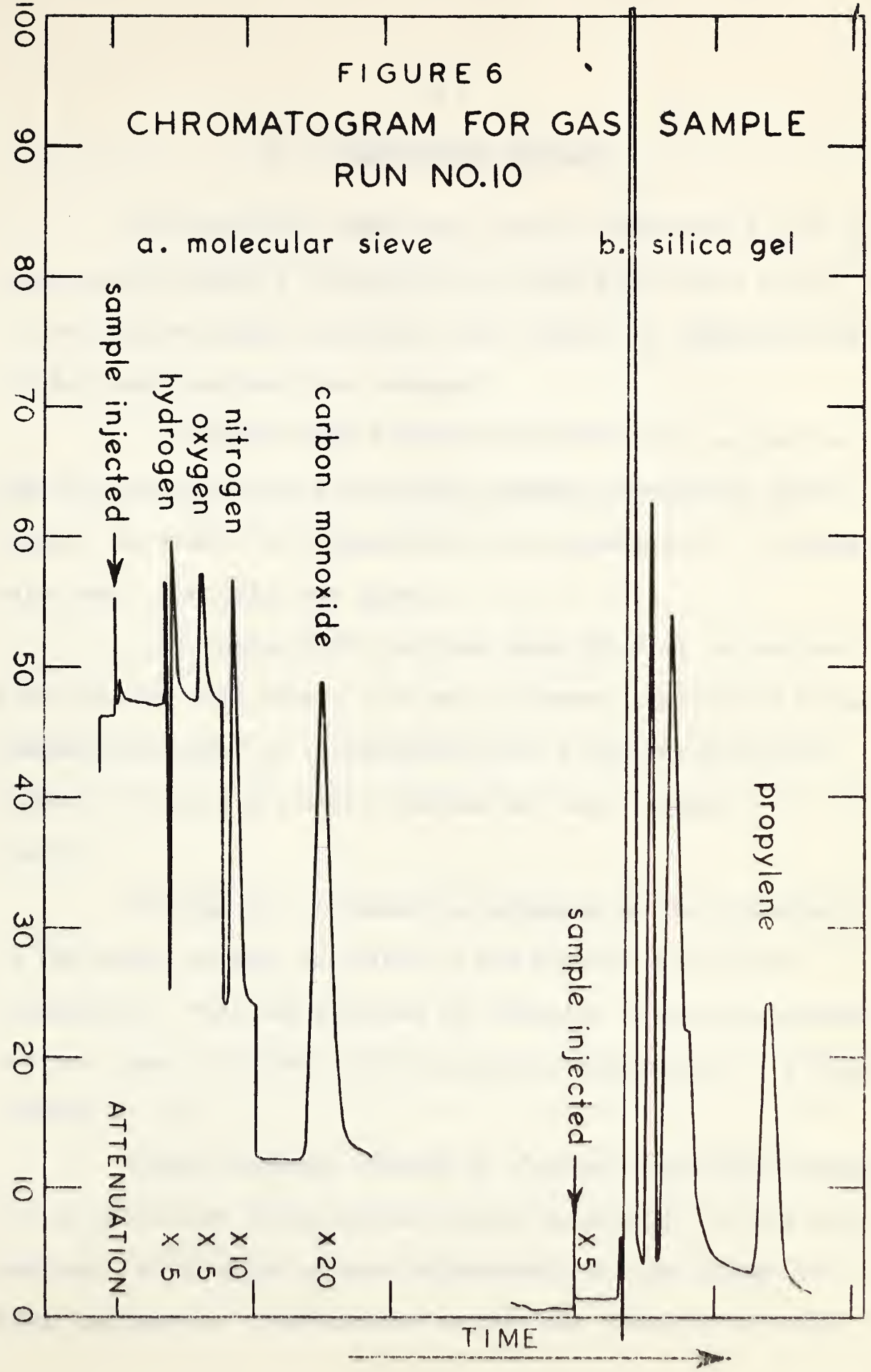


FIGURE 6

CHROMATOGRAM FOR GAS SAMPLE RUN NO.10

VI - EXPERIMENTAL RESULTS

The operating conditions for the experimental runs are summarized in Table I. Each run was carried out for a period of 1/2 hour after steady conditions with respect to temperature and alcohol feed rate had been obtained.

γ-alumina with a surface area 60-70 sq. m./gm. and particle size 1/8 inch x 1/8 inch cylinders supplied by Norton Company was used. It is reported to be predominantly γ-alumina with some α-alumina and quartz.

α-alumina with a surface area 20-30 sq. m./gm. and particle size 3/16 inch x 3/16 inch cylinders supplied by Norton Company was used. It is reported to be α-alumina with some evidence of kappa and delta aluminas and small amounts of quartz.

Chromia on γ-alumina was prepared in the laboratory by the method already described in the section on catalyst preparation. This was analyzed for chromium by spectrophotometry and was found to contain 5.27% chromium corresponding to a Cr_2O_3 content of 7.7%.

Sodium promoted chromia on γ-alumina was also prepared in the laboratory by the method already described. It was also analyzed for chromium by spectrophotometry and for sodium by flame photometry. The chromium content was found to be 5.21%

corresponding to Cr_2O_3 content of 7.61% and the sodium content was found to be 3.2%.

The temperature variation of the bed for runs 1-7 was $\pm$10°C of that reported in Table I while that for runs 8-10 was $\pm$5°C.

Material accountabilities defined as

$$\frac{\text{Weight of liquid products + Weight of gaseous products}}{\text{Weight of n-PrOH fed}} \times 100$$

are included in Table I. Space velocity is defined as $\frac{\text{gms. of n-propanol fed}}{\text{hr. gm. of catalyst}}$. To find the weight of the gaseous products from volume its average molecular weight was obtained from analysis. The unknown components were assigned a molecular weight of 40.

The analysis of liquid and gaseous products are included in Table II. The method adopted for analysis is already explained in the section on analysis of products.

The calculated values for % n-propanol fed appearing in the products as unreacted n-propanol, propionaldehyde, diethyl ketone, di-n-propyl ether and propylene are given in Table III. Also included in Table III are diethyl ketone selectivities and n-propanol conversions. The following definitions have been used for preparing this table.

$$\text{n-PrOH appearing as unreacted n-PrOH} = \frac{\text{moles of n-PrOH in product}}{\text{moles of n-PrOH fed}}$$

$$\text{n-PrOH appearing as PrH} = \frac{\text{moles of PrH formed}}{\text{moles of n-PrOH fed}}$$

$$\text{n-PrOH appearing as DEK} = \frac{2 \times \text{moles of DEK formed}}{\text{moles of n-PrOH fed}}$$

$$\text{n-PrOH appearing as DPE} = \frac{2 \times \text{moles of DPE formed}}{\text{moles of n-PrOH fed}}$$

$$\text{n-PrOH appearing as propylene} = \frac{\text{moles of propylene formed}}{\text{moles of n-PrOH fed}}$$

$$\text{DEK selectivity} = \frac{2 \times \text{moles of DEK formed}}{\text{moles of n-PrOH fed} - \text{moles of n-PrOH in product}}$$

$$\text{n-PrOH conversion} = \frac{\text{moles of n-PrOH in feed} - \text{moles of n-PrOH in product}}{\text{moles of n-PrOH fed}}$$

where n-PrOH is n-propanol

PrH is propionaldehyde

DEK is diethyl ketone

DPE is di-n-propyl ether

Also included in Table III are values for % n-propanol unaccounted for by the known products.

Table I

Operating Conditions and Material Accountability

Run No.	Catalyst	Temp. - °C	Space Velocity hr^{-1}	Feed rate gms/hr	Liquid Product gms	Gaseous Product cu ft at S.T.P.	Material Accountability %
1	I	305	0.965	352	135.3	0.760	95.5
2	I	348	0.795	290	67.6	1.583	88.8
3	I	410	0.630	230	38.0	1.558	90.0
4	II	360	0.700	280	100.5	1.014	98.1
5	II	405	0.510	204	33.1	1.245	82.0
6	III	300	0.520	208	76.0	0.424	89.8
7	III	402	0.470	188	22.3	1.563	90.0
8	IV	370	0.305	122	55.8	1.630	99.9
9	IV	405	0.275	110	45.1	0.343	100.8
10	IV	455	0.270	108	18.9	0.673	88.5

I - γ-alumina

II - α-alumina

III - chromia on γ-alumina

IV - sodium promoted chromia on γ-alumina

Table II

Product Analysis

	Liquid Analysis (weight %)						Gas Analysis (volume %)			
Run No.	n-PrOH	PrH	DEK	DPE	Water*	'Others'	H_2	C_3H_6	CO	'Others'
1	49.20	0.00	0.00	37.80	8.50	4.50	18.0	82.0	0.0	0.0
2	21.00	0.00	0.00	13.05	50.20	15.75	27.0	64.7	0.0	8.3
3	0.00	0.00	0.00	0.00	89.50	10.50	21.2	76.4	0.0	2.4
4	40.30	0.00	0.00	17.00	20.40	22.70	28.2	57.7	0.0	14.1
5	14.90	0.00	0.00	3.30	71.80	10.00	23.8	61.5	0.0	14.7
6	67.40	0.00	0.00	9.90	20.40	2.30	19.3	70.1	0.0	10.6
7	7.05	0.00	0.00	0.00	92.80	0.15	25.9	66.1	0.0	8.0
8	61.80	9.05	1.13	0.00	--	27.84	73.4	2.4	5.4	18.8
9	42.80	13.30	5.13	0.00	--	38.77	72.3	3.0	6.1	18.6
10	8.22	0.00	27.90	0.00	--	63.88	62.5	2.9	20.2	14.4

* estimated

Table III

Product Distribution and Diethyl Ketone Selectivity

	% n-PrOH appearing as							
Run No.	n-PrOH	PrH	DEK	DPE	Propylene	% n-PrOH unaccounted	DEK selectivity %	% n-PrOH conversion
1	37.80	0.00	0.00	34.10	26.80	1.30	0.00	62.20
2	9.84	0.00	0.00	7.18	53.70	29.28	0.00	90.16
3	0.00	0.00	0.00	0.00	78.20	21.80	0.00	100.00
4	28.80	0.00	0.00	14.30	31.60	25.30	0.00	71.20
5	4.83	0.00	0.00	1.26	56.80	37.11	0.00	95.17
6	49.00	0.00	0.00	8.50	21.50	21.00	0.00	51.00
7	2.37	0.00	0.00	0.00	83.20	14.43	0.00	97.63
8	56.50	8.06	1.67	0.00	1.02	32.75	3.83	43.50
9	35.40	11.35	5.91	0.00	2.80	44.54	9.14	64.60
10	3.20	0.00	15.20	0.00	7.39	74.21	15.70	96.80

VII - DISCUSSION OF RESULTS

The present work was planned to investigate the possibility of producing diethyl ketone from n-propanol using chromia catalyst supported on alumina. Since an important requirement for a catalyst carrier is that it should not result in any side reaction it was considered desirable to investigate the activity of alumina itself. γ-alumina had been chosen for reasons already described in the section on literature survey. Experimental runs 1-3 were carried out using γ-alumina. The results clearly show that γ-alumina is very strongly dehydrating and results in the formation of di-n-propyl ether and propylene at lower temperatures while no di-n-propyl ether was found in the products at higher temperature. At 410°C n-propanol conversion was 100% and a small amount of dark brown non-aqueous layer was obtained in the product. The constituents of this liquid could not be identified but its presence does indicate that in addition to dehydration some other side reactions take place which are much slower than dehydration. In these runs both temperature and space velocity were varied simultaneously from run to run. For a comparison of activity it is desirable to vary only one factor at a time. However since the purpose of these experiments was to find whether γ-alumina is active or not runs were carried out at maximum space velocity at which the equipment could be used. As the

temperature was increased, and hence the reaction rate, space velocity had to be decreased to keep the bed at a reasonably constant temperature. It can be concluded that γ-alumina is a very active dehydrating catalyst for n-propanol and may not be a suitable support for the present work. On removing γ-alumina from the reactor a small amount of carbon deposit was found on it.

On reviewing the literature on alumina catalysts it was found that certain alumina preparations are active dehydrating catalysts; dehydrating activity being associated with acid sites on alumina. Since heating alumina to higher temperatures results in loss of acid sites and α-alumina is obtained by heating γ-alumina it was decided to examine the activity of α-alumina. Runs 4 and 5 were carried out with this in view. It is clear from the results that α-alumina also results in the dehydration of n-propanol and gives similar products, namely at lower temperature both di-n-propyl ether and propylene and at higher temperature no di-n-propyl ether. Runs 3 and 5 were carried out at a comparable temperature and may be used to compare the activity of the two aluminas. In run number 3 n-propanol conversion was 100% at a space velocity of 0.63 hr^{-1} while in run number 5 even though the space velocity was 0.51 hr^{-1}, conversion was 95.17%. Thus α-alumina is less active than γ-alumina. However both α- and γ-aluminas are very active dehydrating catalysts and are

not suitable, as such, for the present work. α-alumina was also found to be coated with a small amount of carbonaceous deposit which gave it a grey colour.

When a catalyst is deposited on a support interaction of the two materials is sometimes found to modify the properties of the catalyst. Keeping this in view, further experiments were planned to investigate whether or not the presence of chromia suppressed the dehydrating activity of alumina and simultaneously resulted in the formation of diethyl ketone. A chromia on γ-alumina catalyst was prepared and runs 6 and 7 were carried out with it. This catalyst was also found to result in dehydration of n-propanol but there was no formation of diethyl ketone. The catalyst charged was light brown and presumably was a higher oxide of chromium. On removing the catalyst from the bed it was found to be light green. This change in colour may be associated with the reduction of chromia. This conclusion was further confirmed when sodium was impregnated onto the catalyst from sodium hydroxide solution. While CrO_3 is soluble in NaOH, Cr_2O_3 is not. When an oxidized sample of catalyst, as prepared, was immersed in caustic soda solution an appreciable amount of chromium passed into solution. On the other hand when catalyst removed from the reactor after run number 7 was immersed there was no loss of chromium to the solution.

It was concluded from runs 6 and 7 that this chromia preparation is either not active for the desired reaction or the activity of alumina is so much more as to overshadow the activity of chromia. For further investigation it was decided to make attempts to depress the dehydrating acitivty of alumina. Since the dehydrating activity of alumina is associated with acid sites the catalyst was impregnated with sodium to neutralize the acid sites. Runs 8-10 were carried out with sodium impregnated catalyst. The presence of sodium considerably decreased the dehydration and in addition resulted in the formation of diethyl ketone. Runs 7 and 9 were carried out at substantially the same temperature. In run number 7 the n-propanol conversion was 97.63% at a space velocity of 0.47 hr^{-1} whereas in run number 9 the n-propanol conversion was only 64.60% even though the space velocity was only 0.275 hr^{-1}. The proportion of n-propanol fed dehydrated to propylene in run number 7 was 83.2% as against 2.8% in run number 9. The diethyl ketone selectivity for run number 9 was 9.14 as compared to 0.0% for run number 7. This shows that a considerable improvement in the catalyst can be achieved by impregnating it with sodium.

Runs 8-10 were carried out at a substantially constant space velocity to study the influence of temperature on diethylketone yield. The reaction temperatures were controlled within 5°C of those

reported in Table I. Considering that high conversions of such an endothermic reaction were obtained this temperature control is quite good. The product yields for these runs are plotted as a function of temperature in Figure 7. With increasing temperature the % n-propanol unreacted decreases rapidly, the yield of propionaldehyde goes through a maximum and yield of diethyl ketone increases continuously. The proportion of n-propanol not accounted for by the products of reaction was found to be substantial and increased with temperature. When the liquid product was analyzed using di-n-decyl phthalate on celite column the only peaks registered on the chromatogram were propionaldehyde, n-propanol and diethyl ketone; these taken together accounted for 36 to 62%. Apparently the rest of the sample was retained by the column at the operating conditions used. Changing column conditions did not affect any separation of this material. It is likely that these unidentified compounds in the liquid product result from unaccounted n-propanol. Attempts were made to separate the liquid product into various fractions by batch distillation. However a distillate of continuously increasing temperature was obtained without any separation leaving a dark brown viscous residue at 210°C. Attempts to separate the mixture on Apiezon L on fire brick column were unsuccessful because the separation between the peaks was not good enough to enable the peaks to be trapped to

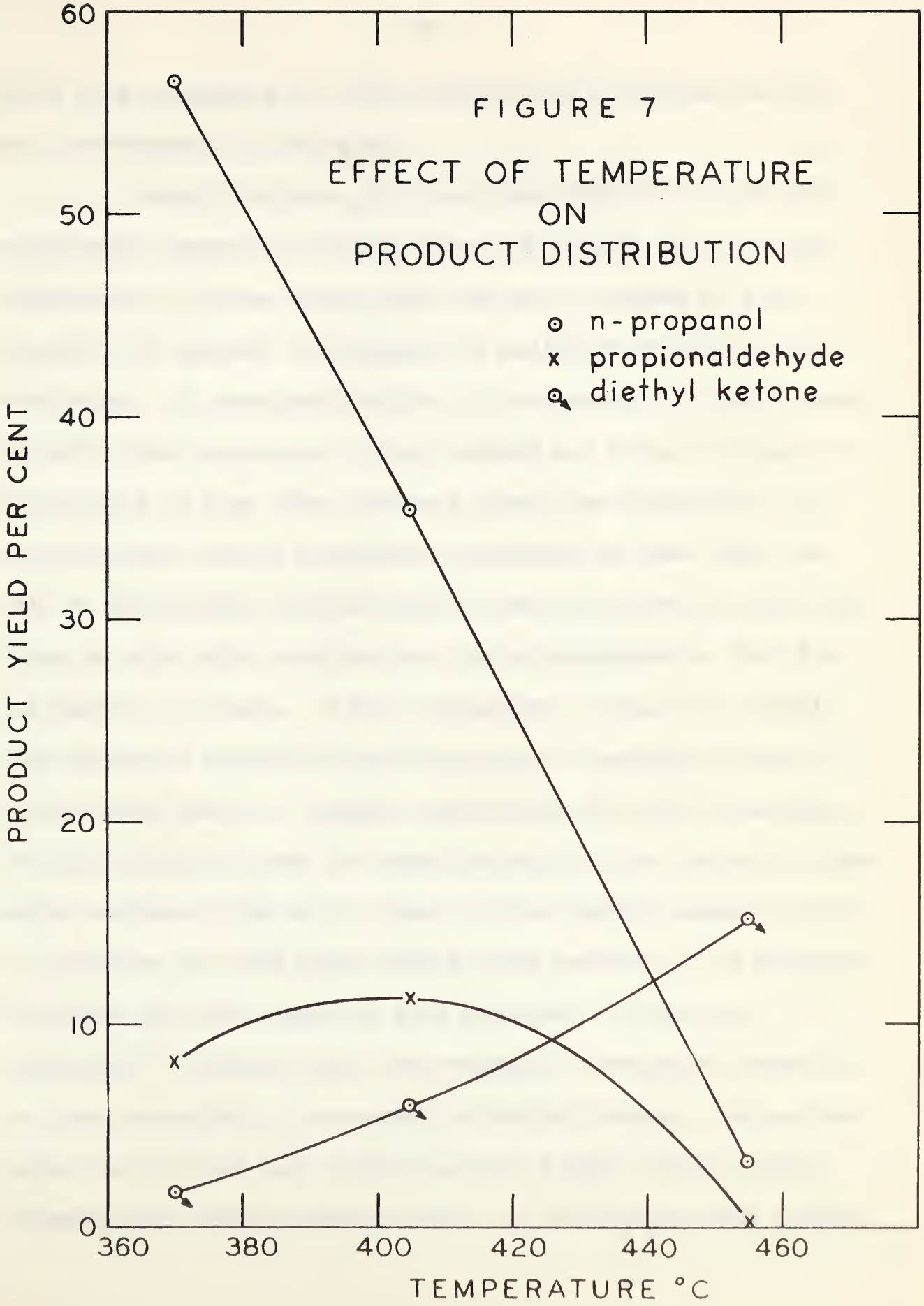


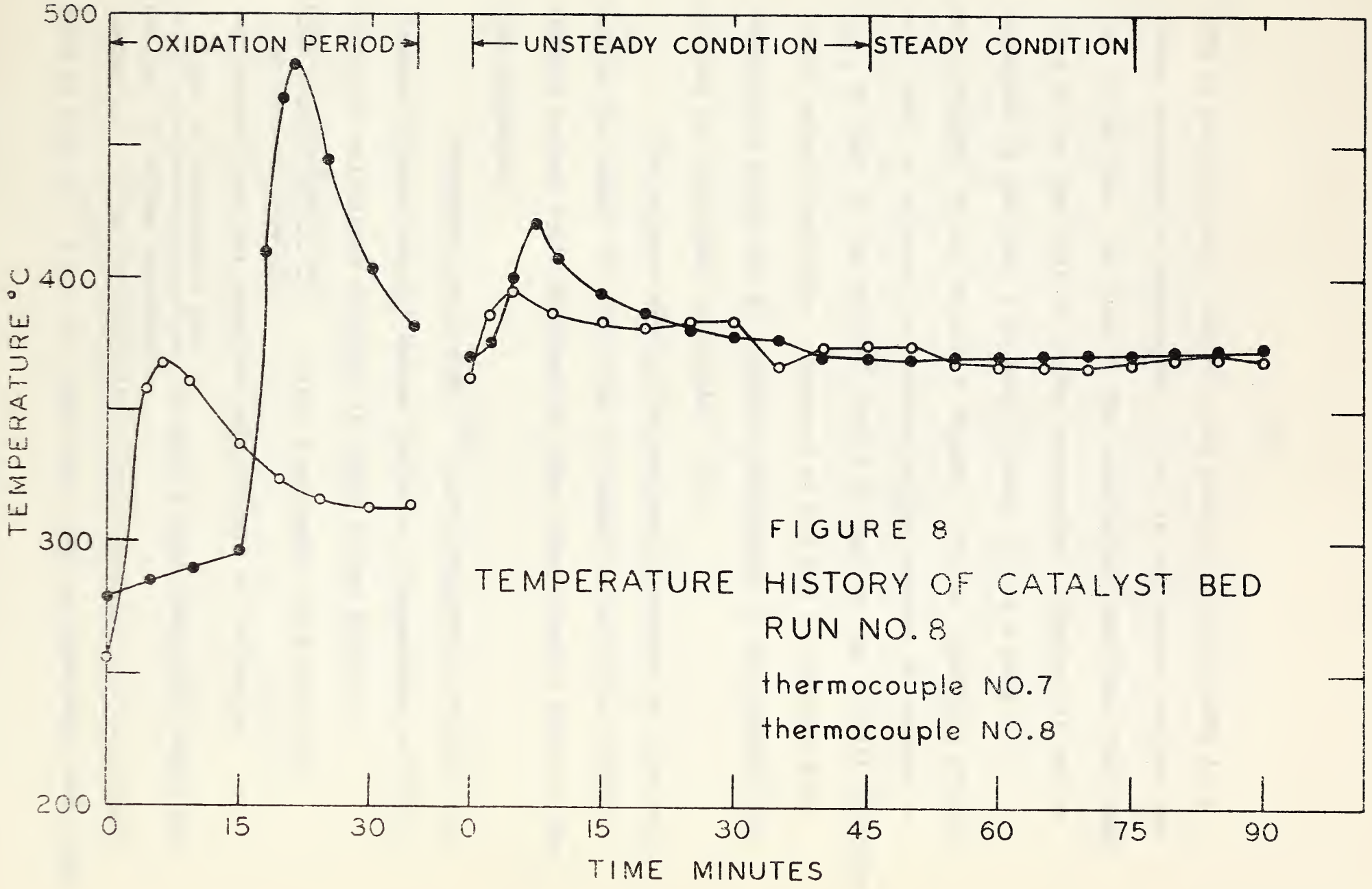
FIGURE 7
EFFECT OF TEMPERATURE
ON
PRODUCT DISTRIBUTION
n-propanol
propionaldehyde
diethyl ketone
PRODUCT YIELD PER CENT
0
10
20
30
40
50
60
360
380
400
420
440
460
TEMPERATURE °C

yield pure components for identification by techniques such as mass spectrometry or infra red.

Though the exact side reactions which result in low selectivity cannot be written unless the unknown products are identified it can be argued that they may be caused by (1) catalyst (2) support (3) presence of sodium or (4) operating conditions. As mentioned earlier, in run number 3 a small amount of dark brown non-aqueous liquid product was formed showing the possibility of some side reactions other than dehydration. In runs 8-10 the rate of n-propanol conversion is lower than the rate of dehydration obtained earlier and it is possible that the rates of other side reactions are quite comparable to that for the desired reaction. If this conjecture is true it is likely that finding a catalyst support inactive to n-propanol would yield better results. Another possibility that may be causing low selectivity is that the space velocity is too low or in other words residence time is too large so that diethyl ketone results in formation of other high boiling point products. The presence of sodium may also result in side reactions. Coley and Komarewsky[5] reported that the presence of sodium was beneficial for the conversion of n-propanol to diethyl ketone. The optimum sodium content was 1.0% indicating that higher sodium content decreased the diethyl ketone yield. In the present work sodium

was impregnated with a view to depress dehydrating activity of alumina. If an inactive catalyst support can be found it may be possible to do away with sodium. In case sodium is required to improve diethyl ketone yield an optimum concentration of this component may be found. However, if chromia itself activates other undesirable side reactions the only possibility is to try other operating conditions namely temperature and space velocity where diethyl ketone yield might be better. For this purpose the equipment will have to be modified so that a wider range of temperatures, and space velocities can be studied.

For runs 6-10 a complete run consisted of bringing the temperature of the catalyst bed to about 250°C, oxidizing it by passing air for about 40 minutes, purging it with nitrogen and starting the alcohol feed. After steady conditions with respect to temperature and n-propanol feed rate had been attained n-propanol feed was continued for 1/2 hour during which time liquid product was collected and gaseous product volume was measured. A typical temperature history of the catalyst bed during a complete experimental run is included in Figure 8. During the oxidation period the temperature of the bed rises and a heat wave passes up the bed starting from the bottom. This large increase in temperature is believed to be partly due to oxidation of Cr_2O_3 to CrO_3 and partly due to oxidation of any adsorbed organic material


500
400
300
200
TEMPERATURE °C
OXIDATION PERIOD
UNSTEADY CONDITION
STEADY CONDITION
0
15
30
0
15
30
45
60
75
90
TIME MINUTES
FIGURE 8
TEMPERATURE HISTORY OF CATALYST BED
RUN NO. 8
thermocouple NO.7
thermocouple NO.8

from an earlier run. When alcohol feed is started there is a sudden increase in temperature, first at the bottom section and then at the top. In view of the endothermic reactions that take place in the bed this is rather unexpected. However it may be explained by the fact that when alcohol is fed a part of it gets oxidized by any adsorbed oxygen, from the oxidation period, and a part is oxidized in reducing higher oxides of chromia to Cr_2O_3 so that in the initial period of the run the overall reactions result in heat evolution. However as the run is continued the temperature drops and by suitable adjustment of the heaters the bed can be controlled to within $\pm$ 5°C.

The highest diethyl ketone yield obtained in this work was in run number 10. In order to compare it with the highest diethyl ketone yield obtained by other investigators Table IV has been prepared.

Komarewsky and Coley[18] used unsupported chromia and obtained highest diethyl ketone yield at a temperature of 425°C. The space velocities reported in Table IV are given as $\frac{\text{gms. of n-propanol fed}}{\text{hr. gm. of catalyst}}$. Since Komarewsky and Coley used unsupported catalyst space velocity should be defined as $\frac{\text{gms. of n-propanol fed}}{\text{hr. gm. of active component}}$ to give a more reasonable basis for comparison. With this definition space velocity used in present work is 3.51 hr^{-1} i.e., 117 times that used by Komarewsky and Coley.

While the n-propanol conversion, diethyl ketone yield and diethyl ketone selectivity obtained in the present work are only slightly better than those obtained by Tollefson[25], these values were obtained at a temperature lower by nearly 70°C which may be considered as a significant technical advantage. As compared to Hansen[12] higher n-propanol conversion, diethyl ketone yield and diethyl ketone selectivity were obtained in the present work at a lower temperature and a higher space velocity.

Table IV

Comparison of Maximum Diethyl Ketone Yields

Investigator	Catalyst	Temperature °C	Space Velocity hr^{-1}	%n-Propanol Conversion	Diethyl Ketone Selectivity %	Diethyl Ketone yield %
Komarewsky (18)	Chromia	425	0.03	95.0	--	48.8
Tollefson (25)	Zinc oxide on alumina	522	0.583	95.1	14.7	14.0
Hansen (12)	Chromia on alumina	475	0.20	68.8	12.7	8.7
This work	Sodium promoted chromia on alumina	455	0.27	96.8	15.7	15.2

VIII - CONCLUSIONS AND RECOMMENDATIONS

1. Two types of alumina, α - and γ-, were found to be very active dehydrating catalysts for n-propanol resulting in the formation of di-n-propyl ether, propylene and water.

2. A chromia on γ-alumina preparation was found to dehydrate n-propanol resulting in the formation of di-n-propyl ether, propylene and water; n-propanol conversions being comparable to those obtained with alumina itself. No diethyl ketone was formed with this catalyst.

3. The presence of sodium in a chromia alumina catalyst considerably depressed the dehydrating activity of the chromia alumina preparation and also resulted in the conversion of n-propanol to diethyl ketone. At 455°C and a space velocity of 0.27 hr^{-1} a 96.8% conversion of n-propanol was achieved; the diethyl ketone yield was found to be 15.2%.

4. It is recommended that this reaction be studied on an unsupported chromia preparation to investigate the extent and nature of side reactions if any.

5. Work should be carried out to find a catalyst support which is inactive with respect to n-propanol. If unsupported chromia catalyst does not result in any side reactions and if an inactive support is found work may then be carried out with a supported chromia preparation.

6. The catalyst bed may be diluted with inert material so that a range of space velocities and possibly higher temperatures can be obtained with the present equipment. This would enable the suggested work to be carried out with the present equipment. However for obtaining kinetic data a more suitable equipment should be built.

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